Electronic Supplementary Information

Diverse binding of important anions in 1-D tricopper coordination polymer (ACP) architectures

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Figure S1. ¹⁹F NMR (228 MHz, acetone $-d_6$ /methanol $-d_4$ (v/v = 1), 298 K) spectra of 2·F, 4·F, 5·F, 6·0.5F·0.5BF₄, KF, and NaBF₄.



Figure S2. Perspective view of cation 1 in $1 \cdot F$ with the atomic numbering scheme (hydrogen atoms are omitted for clarity). Thermal ellipsoids are shown at 30 % probability level.



Figure S3. Perspective view of cation 2 in $2 \cdot F$ with the atomic numbering scheme (hydrogen atoms are omitted for clarity). Thermal ellipsoids are shown at 30 % probability level.



Figure S4. Perspective view of cation 3 in $3 \cdot BF_4$ with the atomic numbering scheme (hydrogen atoms are omitted for clarity). Thermal ellipsoids are shown at 30 % probability level.



Figure S5. Perspective view of cation 4 in $4 \cdot F$ with the atomic numbering scheme (hydrogen atoms are omitted for clarity). Thermal ellipsoids are shown at 30 % probability level.



Figure S6. Perspective view of cation 5 in $5 \cdot BF_4$ with the atomic numbering scheme (hydrogen atoms are omitted for clarity). Thermal ellipsoids are shown at 30 % probability level.



Figure S7. Perspective view of cation 5 in $5 \cdot F$ with the atomic numbering scheme (hydrogen atoms are omitted for clarity). Thermal ellipsoids are shown at 30 % probability level.



Figure S8. Perspective view of cation 5 in $5 \cdot NO_3$ with the atomic numbering scheme (hydrogen atoms are omitted for clarity). Thermal ellipsoids are shown at 30 % probability level.



Figure S9. Perspective view of cation 6 in $6 \cdot 0.5F \cdot 0.5BF_4$ with the atomic numbering scheme (hydrogen atoms are omitted for clarity). Thermal ellipsoids are shown at 30 % probability level.

| | $3 \cdot BF_4$ | 4·F | 5·F | 5·NO ₃ |
|---------------------------------|---------------------------------------|--|---|--|
| Formula | $C_{113}H_{106}BCl_2Cu_3F_4N_4O_4P_6$ | C ₁₀₉ H ₉₈ Cu ₃ FN ₄ O ₃ P ₆ | C ₁₁₃ H ₁₀₄ Cu ₃ FN ₄ O ₂ P ₆ | C ₁₁₃ H ₁₀₄ Cu ₃ N ₅ O ₅ P ₆ |
| M (g/mol) | 2118.16 | 1907.35 | 1945.44 | 1988.45 |
| Crystal system | Triclinic | Monoclinic | Monoclinic | Orthorhombic |
| Space group | <i>P</i> -1 | P2/c | <i>P</i> 21/ <i>m</i> | Pcca |
| a(Å) | 13.946(3) | 19.431(4) | 14.710(3) | 27.9483(3) |
| b (Å) | 14.296(3) | 20.455(4) | 21.288(4) | 21.5782(2) |
| c (Å) | 26.749(5) | 25.426(5) | 19.399(4) | 36.4721(4) |
| α (°) | 81.29(3) | 90 | 90 | 90 |
| β (°) | 77.99(3) | 91.90(3) | 110.49(3) | 90 |
| γ (°) | 81.78(3) | 90 | 90 | 90 |
| Volume (Å ³) | 5121.6(19) | 10100(4) | 5691(2) | 21995.4(4) |
| Ζ | 2 | 4 | 2 | 8 |
| $D_c(g/cm^3)$ | 1.374 | 1.254 | 1.135 | 1.201 |
| Reflections collected | 42615 | 47089 | 35347 | 54383 |
| Independent reflections | 21781 | 19542 | 11308 | 19210 |
| R _{int} | 0.0218 | 0.0451 | 0.0291 | 0.0290 |
| R^a, R^b_w [I>2 σ (I)] | 0.0386, 0.1029 | 0.0519, 0.1371 | 0.0649, 0.2050 | 0.0464, 0.1171 |
| Goodness-of-fit | 1.014 | 1.050 | 1.208 | 1.036 |

Table S1.Crystallographic data for 3·BF₄, 4·F, 5·F, and 5·NO₃.

^a $R = \Sigma(|F_0| - |F_c|) / \Sigma |F_0|$ ^b $R_w = [\Sigma w(|F_0| - |F_c|)^2 / \Sigma w(|F_0|)^2]^{1/2}$

| 1 | ·F | 2·F | 2·F | | |
|--|------------|---------------------|--------------------------|--|--|
| Cu(1)…Cu(2) | 2.5679(9) | Cu(1)…Cu(2) | 2.6127(9) | | |
| $Cu(1)\cdots Cu(3)$ | 2.5870(7) | $Cu(1)\cdots Cu(3)$ | 2.6160(9) | | |
| $Cu(2)\cdots Cu(3)$ | 2.7552(7) | Cu(2)…Cu(3) | 2.5108(9) | | |
| Cu(1) - C(4) | 2.123(3) | Cu(1) - C(4) | 2.274(6) | | |
| Cu(2)–C(4) | 2.228(3) | Cu(2) - C(4) | 2.121(6) | | |
| Cu(3)–C(4) | 2.150(4) | Cu(3) - C(4) | 2.117(6) | | |
| Cu(1) - C(6) | 2.037(4) | Cu(1) - C(6) | 2.100(6) | | |
| Cu(2)–C(6) | 2.264(4) | Cu(2)–C(6) | 2 153(6) | | |
| Cu(3) - C(6) | 2.433(4) | Cu(3)–C(6) | 2 189(6) | | |
| Cu(1) - P(1) | 2.2816(10) | Cu(1) - P(1) | 2 2558(15) | | |
| Cu(1) - P(6) | 2 2870(10) | Cu(1)–P(6) | 2 2798(15) | | |
| Cu(2) - P(2) | 2.2997(11) | Cu(2) - P(2) | 2.2488(16) | | |
| Cu(2) - P(3) | 2.2748(11) | Cu(2) - P(3) | 2.2786(14) | | |
| Cu(3) - P(4) | 2.2710(11) | Cu(3) - P(4) | 2.2700(11) 2.2728(15) | | |
| Cu(3) - P(5) | 2.2030(11) | Cu(3) - P(5) | 2.2728(13) 2 2498(14) | | |
| C(4)-C(5) | 1.198(4) | C(4)–C(5) | 1 208(8) | | |
| C(6) - C(7) | 1.195(5) | C(6)–C(7) | 1.200(0) | | |
| O(1) - C(8) | 1.212(5) | O(1)-C(8) | 1.219(6) | | |
| O(4) - C(9) | 1.200(5) | O(2) - C(9) | 1.237(7) | | |
| O(2) - N(5) | 1.221(5) | C(5)-C(4)-Cu(1) | 121.1(4) | | |
| O(3)–N(5) | 1.228(4) | C(5)-C(4)-Cu(2) | 143.6(5) | | |
| O(5)–N(6) | 1.259(6) | C(5)-C(4)-Cu(3) | 141.6(5) | | |
| O(6)–N(6) | 1.230(6) | C(7)-C(6)-Cu(1) | 136.6(4) | | |
| C(7)-C(6)-Cu(1) | 158.9(3) | C(7)-C(6)-Cu(2) | 140.1(4) | | |
| C(7)-C(6)-Cu(2) | 127.7(3) | C(7)-C(6)-Cu(3) | 130.7(4) | | |
| C(7)-C(6)-Cu(3) | 116.7(3) | Cu(1)-C(4)-Cu(2) | 72.85(19) | | |
| C(5)-C(4)-Cu(1) | 152.6(3) | Cu(1)-C(4)-Cu(3) | 73.04(19) | | |
| C(5)-C(4)-Cu(2) | 125.9(3) | Cu(2)-C(4)-Cu(3) | 72.65(19) | | |
| C(5)-C(4)-Cu(3) | 125.8(3) | Cu(2)-C(6)-Cu(1) | 75.8(2) | | |
| Cu(1)-C(4)-Cu(2) | 72.30(10) | Cu(3)-C(6)-Cu(1) | 75.1(2) | | |
| Cu(1)-C(4)-Cu(3) | 74.52(11) | Cu(2)-C(6)-Cu(3) | 70.64(19) | | |
| Cu(3)-C(4)-Cu(2) | 77.97(11) | | | | |
| Cu(1)-C(6)-Cu(2) | 75.10(12) | | | | |
| Cu(1) - C(0) - Cu(3) Cu(2) - C(6) - Cu(3) | 71 73(10) | | | | |
| Uu(2) - U(0) - Uu(3) | /1./3(10) | | | | |

Table S2. Selected bond lengths (Å) and angles (°) for $1 \cdot F$ and $2 \cdot F$

| 3 · BF ₄ | | <u>4·F</u> | |
|-----------------------------------|------------|---------------------|------------|
| Cu(1)…Cu(2) | 2.5825(9) | Cu(1)…Cu(2) | 2.6028(10) |
| $Cu(1)\cdots Cu(3)$ | 2.5658(10) | $Cu(1)\cdots Cu(3)$ | 2.6618(9) |
| $Cu(2)\cdots Cu(3)$ | 2.6619(8) | Cu(2)…Cu(3) | 2.5769(8) |
| Cu(1) - C(4) | 2.159(2) | Cu(1)-C(4) | 2.320(4) |
| Cu(2) - C(4) | 2.179(2) | Cu(2)-C(4) | 2.078(4) |
| Cu(3) - C(4) | 2.176(2) | Cu(3) - C(4) | 2.148(4) |
| Cu(1) - C(6) | 2.065(2) | Cu(1)-C(6) | 2.067(4) |
| Cu(2)–C(6) | 2.231(2) | Cu(2)–C(6) | 2.282(4) |
| Cu(3) - C(6) | 2.269(3) | Cu(3) - C(6) | 2.210(3) |
| Cu(1) - P(1) | 2.2699(9) | Cu(1) - P(1) | 2.2959(13) |
| Cu(1) - P(6) | 2.2830(10) | Cu(1)–P(6) | 2.2770(12) |
| Cu(2)–P(2) | 2.3006(9) | Cu(2) - P(2) | 2.2749(12) |
| Cu(2) - P(3) | 2.2842(10) | Cu(2) - P(3) | 2.2704(11) |
| Cu(3) - P(4) | 2.2649(10) | Cu(3) - P(4) | 2.2804(11) |
| Cu(3) - P(5) | 2.2851(10) | Cu(3) - P(5) | 2.2637(11) |
| C(4) - C(5) | 1.212(3) | C(4)–C(5) | 1.200(5) |
| C(6)–C(7) | 1.202(3) | C(6)–C(7) | 1.201(5) |
| C(8)–O(1) | 1.224(3) | C(8)–O(1) | 1.193(5) |
| C(9)–O(2) | 1.205(3) | C(9)–O(2) | 1.192(6) |
| C(5)-C(4)-Cu(1) | 137.06(19) | C(5)-C(4)-Cu(1) | 126.1(3) |
| C(5)-C(4)-Cu(2) | 140.4(2) | C(5)-C(4)-Cu(2) | 145.6(3) |
| C(5)-C(4)-Cu(3) | 130.60(19) | C(5)-C(4)-Cu(3) | 134.8(3) |
| C(7)-C(6)-Cu(1) | 156.2(2) | C(7)-C(6)-Cu(1) | 152.3(3) |
| C(7)-C(6)-Cu(2) | 126.6(2) | C(7)-C(6)-Cu(2) | 127.8(3) |
| C(7)-C(6)-Cu(3) | 122.22(19) | C(7)-C(6)-Cu(3) | 124.4(4) |
| Cu(1)-C(4)-Cu(3) | 72.58(8) | Cu(2)-C(4)-Cu(1) | 72.33(11) |
| Cu(1)-C(4)-Cu(2) | 73.07(8) | Cu(3)-C(4)-Cu(1) | 73.01(11) |
| Cu(3)-C(4)-Cu(2) | 75.36(8) | Cu(2)-C(4)-Cu(3) | 75.12(12) |
| Cu(1)-C(6)-Cu(2) | 73.79(8) | Cu(1)-C(6)-Cu(2) | 73.34(11) |
| Cu(1)-C(6)-Cu(3) | 72.43(8) | Cu(1)-C(6)-Cu(3) | 76.90(12) |
| Cu(2)–C(6)–Cu(3) | 72.52(8) | Cu(3)–C(6)–Cu(2) | 70.00(10) |

Table S3. Selected bond lengths (Å) and angles (°) for $3 \cdot BF_4$ and $4 \cdot F$

| 5·F | | 5·BF4 | | | |
|---------------------|------------|---------------------|------------|--|--|
| $Cu(1)\cdots Cu(2)$ | 2.6655(8) | Cu(1)…Cu(2) | 2.5807(9) | | |
| Cu(1)…Cu(1)#1 | 2.5509(9) | $Cu(1)\cdots Cu(3)$ | 2.6265(9) | | |
| Cu(2)…Cu(1)#1 | 2.6654(8) | Cu(2)…Cu(3) | 2.5881(8) | | |
| Cu(1)-C(3) | 2.110(4) | Cu(1) - C(4) | 2.157(4) | | |
| Cu(2) - C(3) | 2.370(5) | Cu(2) - C(4) | 2.321(4) | | |
| Cu(1)#1-C(3) | 2.110(4) | Cu(3) - C(4) | 2.068(4) | | |
| Cu(1) - C(6) | 2.199(4) | Cu(1) - C(6) | 2.147(4) | | |
| Cu(2) - C(6) | 2.089(5) | Cu(2)–C(6) | 2.065(4) | | |
| Cu(1)#1–C(6) | 2.199(4) | Cu(3)–C(6) | 2.382(5) | | |
| Cu(1) - P(1) | 2.2740(10) | Cu(1) - P(1) | 2.2718(12) | | |
| Cu(1) - P(3) | 2.2757(11) | Cu(1) - P(6) | 2.2654(11) | | |
| Cu(2)–P(2) | 2.2672(11) | Cu(2)–P(2) | 2.2741(12) | | |
| Cu(2)–P(2)#1 | 2.2672(10) | Cu(2) - P(3) | 2.2620(12) | | |
| C(3)–C(4) | 1.210(7) | Cu(3) - P(4) | 2.2979(12) | | |
| C(6)-C(7) | 1.168(7) | Cu(3) - P(5) | 2.2662(11) | | |
| C(5)–O(1) | 1.211(8) | C(4)–C(5) | 1.209(5) | | |
| C(8)–O(2) | 1.205(13) | C(7)–C(6) | 1.213(5) | | |
| C(4)-C(3)-Cu(1) | 142.69(9) | C(8)–O(1) | 1.222(5) | | |
| C(4)-C(3)-Cu(2) | 108.8(4) | C(9)–O(2) | 1.215(5) | | |
| C(4)-C(3)-Cu(1)#1 | 142.69(9) | C(5)-C(4)-Cu(1) | 134.5(3) | | |
| C(7)-C(6)-Cu(1) | 133.1(3) | C(5)-C(4)-Cu(2) | 133.0(3) | | |
| C(7)-C(6)-Cu(2) | 139.2(5) | C(5)-C(4)-Cu(3) | 141.2(3) | | |
| C(7)-C(6)-Cu(1)#1 | 133.1(3) | C(7)-C(6)-Cu(1) | 132.3(3) | | |
| Cu(1)–C(3)–Cu(1)#1 | 74.40(16) | C(7)-C(6)-Cu(2) | 139.5(3) | | |
| Cu(1)-C(3)-Cu(2) | 72.76(15) | C(7)-C(6)-Cu(3) | 139.2(3) | | |
| Cu(1)#1-C(3)-Cu(2) | 72.76(15) | Cu(2)-C(4)-Cu(1) | 70.27(12) | | |
| Cu(1)-C(6)-Cu(2) | 76.84(16) | Cu(3)-C(4)-Cu(1) | 76.84(13) | | |
| Cu(1)–C(6)–Cu(1)#1 | 70.92(16) | Cu(2)-C(4)-Cu(3) | 72.01(12) | | |
| Cu(2)-C(6)-Cu(1)#1 | 76.84(16) | Cu(1)-C(6)-Cu(2) | 75.55(13) | | |
| | | Cu(1)-C(6)-Cu(3) | 70.68(13) | | |
| | | Cu(3)-C(6)-Cu(2) | 70.77(13) | | |

Table S4. Selected bond lengths (Å) and angles (°) for $5 \cdot F$ and $5 \cdot BF_4$

Symmetry Code: #1: x,-y+1/2,z

| 5·NO ₃ | | 6·0.5F·0.5BF ₄ | |
|---------------------|-----------|---------------------------|------------|
| $Cu(1)\cdots Cu(2)$ | 2.6038(5) | $Cu(1)\cdots Cu(2)$ | 2.5574(7) |
| $Cu(1)\cdots Cu(3)$ | 2.5861(5) | $Cu(1)\cdots Cu(3)$ | 2.6727(7) |
| $Cu(2)\cdots Cu(3)$ | 2.6171(5) | $Cu(2)\cdots Cu(3)$ | 2.6566(6) |
| Cu(1)-C(4) | 2.255(3) | Cu(1)-C(4) | 2.149(5) |
| Cu(2)–C(4) | 2.104(3) | Cu(2) - C(4) | 2.088(4) |
| Cu(3)-C(4) | 2.140(3) | Cu(3)-C(4) | 2.381(4) |
| Cu(1)-C(6) | 2.086(3) | Cu(1)-C(6) | 2.272(4) |
| Cu(2)–C(6) | 2.350(3) | Cu(2)–C(6) | 2.213(4) |
| Cu(3)-C(6) | 2.199(3) | Cu(3) - C(6) | 2.092(4) |
| Cu(1) - P(1) | 2.2654(8) | Cu(1) - P(1) | 2.2846(11) |
| Cu(1)–P(6) | 2.2845(8) | Cu(1)–P(6) | 2.2686(11) |
| Cu(2)–P(2) | 2.3084(7) | Cu(2)–P(2) | 2.2940(11) |
| Cu(2) - P(3) | 2.2810(7) | Cu(2)–P(3) | 2.2745(13) |
| Cu(3) - P(4) | 2.2665(7) | Cu(3) - P(4) | 2.2885(12) |
| Cu(3)–P(5) | 2.2890(8) | Cu(3) - P(5) | 2.2989(10) |
| C(4)–C(5) | 1.218(4) | C(4)–C(5) | 1.215(6) |
| C(7)–C(6) | 1.217(4) | C(6)–C(7) | 1.202(6) |
| C(8)–O(1) | 1.207(4) | C(8)–O(1) | 1.222(6) |
| C(9)–O(2) | 1.216(4) | C(9)–O(3) | 1.224(5) |
| C(5)-C(4)-Cu(1) | 125.6(2) | C(5)-C(4)-Cu(1) | 134.2(4) |
| C(5)-C(4)-Cu(2) | 143.9(2) | C(5)-C(4)-Cu(2) | 151.0(4) |
| C(5)-C(4)-Cu(3) | 136.0(2) | C(5)-C(4)-Cu(3) | 116.6(3) |
| C(7)-C(6)-Cu(1) | 145.3(2) | C(7)-C(6)-Cu(1) | 127.0(4) |
| C(7)-C(6)-Cu(2) | 139.3(2) | C(7)-C(6)-Cu(2) | 132.6(3) |
| C(7)-C(6)-Cu(3) | 124.5(2) | C(7)-C(6)-Cu(3) | 145.9(3) |
| Cu(2)-C(4)-Cu(1) | 73.26(8) | Cu(2)-C(4)-Cu(1) | 74.24(15) |
| Cu(3)-C(4)-Cu(1) | 72.05(8) | Cu(1)-C(4)-Cu(3) | 72.11(13) |
| Cu(2)-C(4)-Cu(3) | 76.14(9) | Cu(2)-C(4)-Cu(3) | 72.60(13) |
| Cu(1)-C(6)-Cu(2) | 72.05(8) | Cu(2)-C(6)-Cu(1) | 69.52(11) |
| Cu(1)-C(6)-Cu(3) | 74.17(9) | Cu(3)-C(6)-Cu(1) | 75.41(13) |
| Cu(3)-C(6)-Cu(2) | 70.15(8) | Cu(3)-C(6)-Cu(2) | 76.17(14) |

Table S5. Selected bond lengths (Å) and angles (°) for $5 \cdot NO_3$ and $6 \cdot 0.5F \cdot 0.5BF_4$



Figure S10.Two independent *meso*-helical chains linked by NO₂…NO₂ interactions in the anion coordination polymer (ACP) **1**·**F**. View along the *b*-axis (a).Intermolecular NO₂…NO₂ interactions in **1**·**F** (b).



Figure S11. Anion coordination environment in anion coordination polymer (ACP) $4 \cdot F$ (green: F; red: O; black: C; blue: N; white: H). Only use groups and anions are shown for clarity.



Figure S12. Anion coordination environment in anion coordination polymer (ACP) **5**•**F** (green: F; red: O; black: C; bule: N; white: H). Only urea groups and anions are shown for clarity.

| Compound | D–H…A | D–H (Å) | H…A (Å) | D…A (Å) | ∠ DHA(°) | Symmetry Code |
|---------------------------|-------------------------|---------|---------|-----------|----------|---------------|
| $3 \cdot BF_4$ | N(1)- $H(1A)$ ···F(1) | 0.88 | 1.97 | 2.845(3) | 171.3 | |
| | N(2)-H(2A)…F(2) | 0.88 | 2.40 | 3.236(4) | 158.1 | |
| | $N(2)-H(2A)\cdots F(1)$ | 0.88 | 2.50 | 3.273(4) | 147.4 | |
| | N(3)-H(3A)…F(2)#1 | 0.88 | 2.11 | 2.964(3) | 165.0 | x – 1, y–1, z |
| | N(4)-H(4A)…F(3)#1 | 0.88 | 2.05 | 2.916(3) | 166.3 | x – 1, y–1, z |
| 4 • F | N(1)-H(1A)…F(1)#1 | 0.88 | 1.96 | 2.784(5) | 154.5 | x, y– 1, z |
| | N(2)-H(2A)…F(1)#1 | 0.88 | 1.93 | 2.760(5) | 157.0 | x, y– 1, z |
| | N(3)-H(3A)…F(1) | 0.88 | 2.00 | 2.720(5) | 138.4 | |
| | N(4)- $H(4A)$ ···F(1) | 0.88 | 1.95 | 2.757(6) | 151.8 | |
| 5·F | N(1)-H(1)-F(1) | 0.88 | 1.74 | 2.613(7) | 174.1 | |
| | N(2)-H(2)-F(1) | 0.88 | 2.27 | 3.051(9) | 147.7 | |
| | N(3)-H(3)…F(1)#2 | 0.88 | 1.74 | 2.527(9) | 147.3 | 2x-1, y, z-1 |
| | N(4)-H(4)…F(1)#2 | 0.88 | 2.13 | 2.794(9) | 132.2 | 2x-1, y, z-1 |
| 6·0.5F·0.5BF ₄ | N(1)-H(1A)…F(2B) | 0.88 | 2.29 | 3.099(16) | 153.5 | |
| | N(1)-H(1A)…F(2A) | 0.88 | 2.44 | 3.188(15) | 143.2 | |
| | N(2)-H(2A)…F(2A) | 0.88 | 1.88 | 2.757(13) | 173.5 | |
| | N(3)-H(3A)…F(1) | 0.88 | 2.25 | 2.990(3) | 142.0 | |

Table S6. Selected hydrogen bonding parameters for 3·BF₄, 4·F, 5·F, and 6·0.5F·0.5BF₄



(b)



Figure S13. Four independent 1-D linear chains found in anion coordination polymer (ACP) $2 \cdot F$ (view from the top of 1-D chains (a); view alone the 1-D chains (b)).



(b)



Figure S14. Four independent 1-D linear chains in anion coordination polymer (ACP) **4**•**F** (view from the top of 1-D chains (a); view alone the 1-D chains (b)).



Figure S15. Two independent 1-D linear chains in anion coordination polymer (ACP) **5**•**F** (view from the top of 1-D chains (a); view along the 1-D chains (b)).



Figure S16. Two independent 1-D linear chains in anion coordination polymer (ACP) $3 \cdot BF_4$ (view from the top of 1-D chains (a); view along the 1-D chains (b)).



Figure S17. Anion coordination environment (BF_4^- (a) and F^- (b)) in anion coordination polymer (ACP) **6**•**0.5F**•**0.5BF**₄ (green: F; red: O; black: C; bule: N; white: H; brown: B). Only urea groups and anions are shown for clarity.

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Figure S18. UV-vis electronic absorption spectrum of $1 \cdot F$ in the solid state at room temperature.



Figure S19. UV-vis electronic absorption spectrum of $2 \cdot F$ in the solid state at room temperature.



Figure S20. UV-vis electronic absorption spectrum of $3 \cdot BF_4$ in the solid state at room temperature.



Figure S21. UV-vis electronic absorption spectrum of $4 \cdot F$ in the solid state at room temperature.



Figure S22. UV-vis electronic absorption spectrum of $5 \cdot F$ in the solid state at room temperature.



Figure S23. UV-vis electronic absorption spectrum of $5 \cdot BF_4$ in the solid state at room temperature.



Figure S24. UV-vis electronic absorption spectrum of $5 \cdot NO_3$ in the solid state at room temperature.



Figure S25. UV-vis electronic absorption spectrum of $6.0.5F.0.5BF_4$ in the solid state at room temperature.



Figure S26. Emission spectra of $2 \cdot F$ in the solid state at 298 K (a) and 77 K (b) ($\lambda_{ex} = 300 \text{ nm}$).



Figure S27. Emission spectra of $3 \cdot BF_4$ in the solid state at 298 K (a) and 77 K (b) ($\lambda_{ex} = 300$ nm).



Figure S28. Emission spectra of $4 \cdot F$ in the solid state at 298 K (a) and 77 K (b) ($\lambda_{ex} = 300 \text{ nm}$).



Figure S29. Emission spectra of $5 \cdot F$ in the solid state at 298 K (a) and 77 K (b) ($\lambda_{ex} = 300$ nm).



Figure S30. Emission spectra of $5 \cdot BF_4$ in the solid state at 298 K (a) and 77 K (b) ($\lambda_{ex} = 300$ nm).



Figure S31. Emission spectra of $5 \cdot NO_3$ in the solid state at 298 K (a) and 77 K (b) ($\lambda_{ex} = 300 \text{ nm}$).



Figure S32. Emission spectra of $6 \cdot 0.5F \cdot 0.5BF_4$ in the solid state at 298 K (a) and 77 K (b) ($\lambda_{ex} = 300$ nm).